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MODELING HYDROGEN GENERATION RATES IN THE HANFORD WASTE TREATMENT AND IMMOBILIZATON PLANT

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INTRODUCTION

Hanford Site and Environmental Management Science Program investigators are working together to address issues concerning hydrogen generation rates in the Hanford waste treatment and immobilization plant (WTP). The hydrogen generation rates of radioactive wastes must be estimated to provide for safe operation of the plant: for example, to determine the amount of ventilation needed to avoid accumulation of flammable concentrations of H_2 in the headspaces of process vessels; also, to determine in which vessels and how quickly H_2 may accumulate in the event of power failure or emergency shutdown.

Hanford tank wastes are generally complex, multi-phase, highly concentrated solutions containing many of the elements in the periodic table. This is because the wastes have been subjected to many operations (*e.g.*, chemical separations and evaporation), mixing and aging. The production of hydrogen in these waste materials results from radiolysis of water and the thermolysis and indirect radiolysis of organic compounds. Each of these processes is complex. However, substantial amounts of work were funded by the Department of Energy to understand these processes well enough to ensure that the tank waste storage farms are operated safely.[1]

As part of that effort, Albert Hu developed a correlation for predicting hydrogen generation rates in the wastes stored at the Hanford Tank Farms.[2,3] It is based on a chemical model for hydrogen production by thermal and radiolytically-induced processes. In brief, it predicts the radiolytic component of the hydrogen generation rate from the radioactive decay heat, temperature and the total organic carbon (TOC) concentration with adjustments for the scavenging of hydrogen atoms and electrons by nitrate and nitrite ions. The thermal component of hydrogen generation is related to the concentrations of aluminum (a catalyst) and TOC and the temperature. The model was benchmarked with data obtained from the Tank Farms[2], it was applied to the Hanford Tank Farms[4] and ultimately, it was used to close out the Flammable Gas Safety Issue.[5] Subsequently, it has also been used for waste in other configurations at the Tank Farms[3,6,7].

While the Hu model satisfactorily predicts rates for quiescent wastes in Hanford underground storage tanks, pretreatment operations will alter the conditions and chemical composition of these wastes. The waste will be initially diluted, later concentrated and separated into high-solids and liquid fractions and recombined as a slurry enriched with radionuclides (^{137}Cs). These operations will introduce reagents, redistribute species and suspend solids; different phases will be introduced in common vessels and then mixed; temperatures will be changed at various rates through heating, cooling or heat transfer. Therefore, it is necessary to determine the applicability of the Hu model to waste streams in the WTP.

Each unit operation of the WTP was evaluated to determine whether the waste stream chemical composition was within the boundary conditions of the Hu correlation.[8] It was concluded that the chemical model is generally applicable to the Hanford Waste Treatment and Immobilization Plant. However, the review identified some specific concerns that required study. The concerns arise when WTP processing steps produce conditions outside the range of conditions used to parameterize the Hu model. The concerns include effects of saturation with air (oxygen) from pulse-jet mixing, *alpha* radiolysis, treatment with potassium permanganate, adding hydroxide ion or acidifying the wastes, organic compounds from degraded ion exchange resins, sucrose additions and addition of glass-former chemicals. The effects of these conditions are being systematically investigated through literature review, technical analyses and experimental work. These issues and the status of the work to date are the topic of the presentation. What follows is a brief description of each concern and the path taken to resolve it.

<u>Effect of Saturating Waste With Air</u>

The Hu correlation[9,2,4] was devised for quiescent wastes that are not mixed with air during interim storage. In contrast, operations at the WTP will be aerated by pulse-jet mixing and therefore oxygen will be introduced into the wastes. Previous work with wastes and waste simulants have shown that oxygen may increase hydrogen generation rates, in some cases by an order of magnitude. The mechanism of the effect is not well understood, but it appears to mainly alter and enhance thermal degradation pathways that produce hydrogen. As the Hu model was parameterized to predict

hydrogen generation rates from stored tank wastes which are depleted in oxygen, it was decided to perform experimental tests with some representative Hanford tank wastes exposed to oxygen cover gas to quantify the impact of oxygen on hydrogen production in these wastes. These tests are currently in progress and results will be described at the meeting.

Effect of *Alpha* Radiation

The Hu correlation[9,2,4] does not consider the influence of *alpha* radiation on the hydrogen generation rate because the concentrations of these emitters are much smaller than the concentrations of the *beta* and *gamma* emitters in tank waste and because the *alpha* emitters are concentrated in sludges where the particles have very short ranges. The flow sheet analysis indicated that the situation in the WTP differs because the *alpha* emitters will be concentrated in preparation for vitrification. Therefore, it is not evident that their role in hydrogen generation can be neglected.

The literature on generation of H_2 by *alpha* radiolysis was reviewed. No publications about the alphia radiolysis of alkaline solutions of Hanford Site waste were found. However, *alpha* radiolysis of nitric acid solutions and *alpha* radiolysis of neutral solutions of scavengers were very relevant. Several authors had measured the value of $G(H_2)$ for the *alpha* radiolysis of nitric acid.[10,11,12] More recently, LaVerne and coworkers[13,14] at Notre Dame Radiation Laboratory reinvestigated hydrogen generation by *alpha* radiolysis of water containing a variety of electron scavengers including nitrate and nitrite ions. With the insights provided by their work, we adapted the Hu model to account for effects of alipha radiolysis in wastes. Further details will be provided in the presentation.

Effect of Treating With Potassium Permanganate

An Ultra-filtration Process in the WTP will add sodium permanganate to remove Sr/TRU before the filtration operation. The permanganate ion is a potent oxidizer of organic compounds. The impact of permanganate addition to Hanford waste feed in the WTP was therefore identified as a potential concern for applying the Hu correlation to predict hydrogen generation, because organic compounds dominate the behaviors described by the correlation. The effects of permanganate additions to Hanford Envelope C waste have been studied in experimental tests using simulants and actual waste.[15,16,17] We analyzed the results of these tests to assess the potential effect on hydrogen generation rates. Our analyses suggest that that permanganate is not likely to accelerate any of the processes responsible for hydrogen production.

When added to the waste, permanganate is rapidly reduced to lower oxidation states of manganese, primarily Mn(IV). Experimental data suggest that the organic compounds present in the wastes are the main reductants for permanganate,[18] but the total organic carbon content (TOC) is not significantly impacted, because the levels of permanganate are relatively low (0.075 M) compared to the levels of TOC in wastes (~1 M) destined for treatment with permanganate. Nonetheless, organic complexants are partially oxidized by the permanganate addition. The resulting compounds, being more oxidized, are expected to generate less hydrogen. Otherwise, addition of permanganate ion produces

little chemical change in the supernatant fraction of the waste. The Mn(IV) compounds precipitate from solution and are removed by filtration. As a result, the filtered solids contain a significantly higher concentration of Mn than the initial entrained solids. The Hu model should be as valid for permanganate treated wastes as it is for the untreated waste.

Effect of Sodium Hydroxide Addition

Hydroxide ion plays an important role in the chemistry associated with hydrogen generation in Hanford waste. Because of this and the fact that the Ultrafiltration Process will involve addition of large quantities of sodium hydroxide, concerns were raised for applying the Hu model to the WTP. A review of the relevant literature suggests that even though the concentration of hydroxide is not a key parameter in Hu's model, large additions are not likely to invalidate use of Hu's model at the WTP. Detail explanations will be provided in the presentation. Here, we mention that in developing the correlation, Hu used data from 15 of Hanford tanks in which hydroxide concentrations were in excess of 3 M and supporting laboratory experiments involved concentrations up to 6 M. Without a concurrent effect of oxygen, varying the hydroxide concentration should not impact the ability of the Hu correlation to provide hydrogen generation rates to within its stated accuracy (±300%).

Effect of Acidifying the Waste

Effect of acidification of the waste in the Cs Ion Exchange Process, Ultrafiltration Process and any off-normal events will reduce the pH of the waste. The Hu correlation was developed for the alkaline conditions in the Hanford waste tanks. *A priori*, it is not expected to be applicable to acidic wastes. Experimental testing is in progress to determine HGRs expected during these processing steps and to establish whether new catalytic actions are initiated in the acidic regime.

Effects of Organic Compounds Added During Processing

Hydrogen production from organic compounds is understood well enough to provide bounding assessments of whether "new" organics (*e.g.*, ion exchange resin and associated degradation products and sucrose) may impact the Hu correlation's ability to predict hydrogen generation rates within the accepted uncertainty of the model.

Sucrose will be added to the waste stream to accomplish denitrification of the waste in the cold cap of the melter. The Hu correlation is focused on waste streams that are rich in organic complexants. The tank wastes have had significant quantities of glycolate ion and gluconate added to them and butanol from hydrolysis of tributyl phosphate that entered the tank wastes from the PUREX process.[19] Sugar is expected to behave chemically like these constituents. Soluble TOC is a variable in the Hu model. Therefore, it should suffice to combine the TOC from sugar with soluble TOC in the waste to predict the effect of added sugar.

Concerns were also raised that some waste streams may contain degradation products of the organic ion exchange materials. In particular, there was concern about the nitric acid eluate that would also be rich in ^{137}Cs. However, this stream is destined to be

concentrated to several molar nitric acid in a reduced pressure evaporator. These conditions should completely degrade remnants of organic resins and other organic compounds so that downstream effects are expected to be negligible.

Effects of Glass Formers

Glass-forming minerals will be introduced in the HLW Vitrification Melter Feed Preparation Process. Some of these substances may catalyze the radiolytic generation of hydrogen. Metallic particles in water, hydrated oxide powders and aqueous suspensions of silica nanoparticles have all been noted to catalyze water radiolysis and increase the yield of H_2.[20] However, LaVerne and Tonnies[20] studied the effect of silica particle size on the yields of H_2 and concluded that the effect in solution is limited to very small particles. Therefore, it appears that particle sizes of glass former compounds to be added in the WTP streams would be too large to significantly catalyze hydrogen production. Nevertheless, a full evaluation of this issue is in progress.

SUMMARY/CONCLUSION

An evaluation of the WTP flowsheet was performed to determine the applicability of the Hu correlation to predict hydrogen generation in the WTP. The evaluation concluded that while applicable to many of the unit operations in the plant, the physical/chemical conditions for several process operations deviate from the conditions for which the model was parameterized. Additional work was required to ascertain whether the Hu model was applicable, whether it could be adapted or whether experimental tests should be performed. In some cases, *e.g.*, the effect of hydroxide ion and permanganate additions and *alpha* radiolysis, the issues can be concluded by technical analyses of documented results and through chemical kinetic simulations. In other cases, *e.g*. the effects of oxygen saturation and acidification of the wastes, resolution required that experimental tests be performed. Some of the above cases, *e.g.*, *alpha* radiolysis, require the model to be adapted, others, *e.g.*, acidification of the waste, may require substitute models or be guided by results of experimental tests that are in progress.

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